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**ENVIRONMENTAL FATES AND IMPACTS OF  
MAJOR FOREST USE PESTICIDES**

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Common Name: Triclopyr  
Chemical Name: 3,5,6-trichloro-2-pyridinyloxyacetic acid  
Major Trade Names: Garlon 3A; Garlon 4  
Major Applications in Forestry: Used on an experimental basis in the Northeast, the Pacific Northwest and the South, primarily in site preparation and occasionally in conifer release for woody plant and broadleaf weed control.

#### SUMMARY

Triclopyr is a relatively new herbicide which has been commercially available only in the past few years. Accordingly, very little data are available in connection with its efficacy and environmental fate and impacts. The limited available data are largely from laboratory and/or field studies conducted by the manufacturer on non-forest systems.

The mechanism of triclopyr uptake by plants is through both leaves and roots. It induces characteristic auxin-type responses in plants. Triclopyr is not considered a persistent compound in soils; it degrades rapidly, with an average half-life of 46 days. The major route of degradation in soil is via microbial decomposition. Degradation of triclopyr does not occur to any appreciable extent via chemical hydrolysis or other chemical routes in soil. Triclopyr losses due to volatilization are not appreciable.

Triclopyr is considered a mobile herbicide. Leaching and desorption are lowest in soils with high organic matter content. Because of its mobility and rapid desorption from soil particles, some loss of triclopyr due to solubilization and/or runoff may be expected following field application. Although it is stable to hydrolysis in aqueous solution, triclopyr photo-degrades rapidly with a half-life of 10 hours at 25°C.

Triclopyr can cause injury to conifers, particularly at high rates of application and is not generally recommended for conifer release. When applied directly, it exhibits phytotoxicity to agricultural crops. Triclopyr has low toxicity to fish and lower aquatic organisms and does not bioaccumulate in these species. It exhibits low toxicity to wildlife and is considered non-toxic to soil microorganisms.

## 1.0 INTRODUCTION

Triclopyr is an auxin-type herbicide for the control of many woody plants and annual and perennial broadleaf weeds. It has only recently been registered for use in forestry and it is used primarily on experimental rather than commercial scales for site preparation (1,2,3) and occasionally in conifer release (4,5). These uses are in the Northeast, the Pacific Northwest, and the South (5,6). It is not registered for use in California (3). No quantitative data are available on the extent of the uses in the Northeast and South, although it is estimated that about 100 acres in Washington, Oregon and California were treated with triclopyr in 1979 (about only 5 of the 100 acres were in California) (3). Due to production capacity limitation, the use of triclopyr in certain regions has been restricted by the manufacturer (Dow Chemical Co.) to extend the supply and make it available to new potential users (3). Most current experimental uses in the Pacific Northwest are ground applications for stump treatment and tree injection (4,7). Recommended rates for aerial spraying are 2-3 gallons/acre (Garlon 3A) for broadcast application by low-volume ground or helicopter equipment, and one-half to one gallon/100 gallons water for high volume, full spray coverage (4,8). Triclopyr may be used in combination with 2,4-D, Tordon 101, Esteron 99, or DMA 4 for forest site preparation (1,9,10).

According to the manufacturer, triclopyr is effective for the control of the following woody species: alder, arrowwood, ash, aspen, beach, birch, blackberry, blackgum, cascara, chamise, choke cherry, cottonwood, crataegus (hawthorn), dogwood, elderberry, elm, hazel, hickory, hornbeam, locust, maples, mulberry, oaks, persimmon, pine, poison oak, poplar, salmonberry, sassafras, sumac, sweetbay magnolia, sweetgum, sycamore, thimbleberry, tulip poplar, willow, and winged elm (1,11). Among the annual and perennial broadleaf weeds controlled are: burdock, chicory, curled dock, dandelion, field bindweed, lambsquarters, plantain, ragweed, smartweed, vetch and wild lettuce (1). It is not effective for control of most grasses.

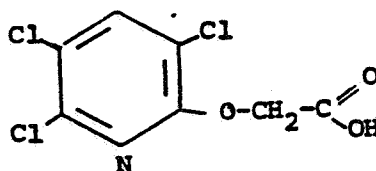
Triclopyr is also recommended for the control of woody and herbaceous weeds in non-crop areas including industrial manufacturing and storage sites, and rights-of-way such as electric power lines, communication lines, pipelines, roadsides and railroads. Triclopyr induces characteristic auxin-type

responses in plants (8); i.e., it regulates longitudinal cell structure so as to control bending of the stalk or stem in phototropic responses (12). It is absorbed by both leaves and roots, and is readily translocated through the plant (8). Maximum plant response is achieved when application is made soon after full leaf development (8).

Triclopyr is manufactured by Dow Chemical USA, Ag-Organics Dept. (13). It is produced in two major formulations (8): Garlon 3A and Garlon 4. Garlon 3A contains 44.4 percent active ingredient as the triethylamine (TEA) salt, which is equivalent to 31.8 percent acid equivalent and is present in the formulated product at 3 lbs acid equivalent/gallon. This water-soluble formulation also contains methanol. Garlon 3A is also available as Experimental Herbicide M-3724 in areas where the Garlon 3A label has not been approved (8). Garlon 4 is an oil-soluble water-emulsifiable ethylene glycol butyl ether ester (EGBE) formulation containing 4 lbs of triclopyr acid equivalent/gallon (8). Surfactants may be added to Garlon 3A formulations to improve its effectiveness (1). Water is the usual carrier for foliar sprays; fuel oil is used for basal sprays (14).

## 2.0 PHYSICAL/CHEMICAL PROPERTIES OF ACTIVE INGREDIENT

The active ingredient of triclopyr is 3,5,6-trichloro-2-pyridinyloxy-acetic acid:



It is a white, odorless solid with melting point of 148-150°C. Solubility in various solvents at 25°C is (14):

<u>Solvent</u>	<u>g/ml</u>	<u>Solvent</u>	<u>g/ml</u>
Acetone	98.9	n-hexane	0.041
Acetonitrile	12.6	n-octanol	30.7
Benzene	2.73	Xylene	2.79
Chloroform	2.73	Water	0.043

Vapor pressure data are shown below as a function of temperature (14):

<u>Temperature</u>	<u>mm Hg</u>
25	$1.26 \times 10^{-6}$
40	$5.30 \times 10^{-6}$
50	$1.03 \times 10^{-5}$
70	$1.04 \times 10^{-4}$

### 3.0 ENVIRONMENTAL FATE

Being a very new pesticide, the fate of triclopyr in the environment (especially the forest environment) following application has not been the subject of much scientific investigation. The very limited data which have been reported are from studies performed or sponsored by the manufacturers and pertain to non-forest environments.

#### 3.1 UPTAKE AND METABOLISM BY PLANTS

Limited studies have been conducted on the uptake of triclopyr by plants. As noted previously, it induces auxin-type responses in plants. It is adsorbed by both leaves and roots, and is readily translocated throughout the plant (8).

The effects of photoperiod and temperature on the translocation of triclopyr were studied by Radosevich and Bayer (15) on tanoak, snowbrush ceanothus, bigleaf maple, beans and barley. Translocation of triclopyr was observed to be greatest under warm temperatures and long-day photoperiods. With colder temperatures and short-day photoperiods, movement was greatly reduced. Following application directly to leaves, triclopyr was observed to move readily in the symplasts, with the preponderance remaining in the shoot. Applications to the roots resulted in very little apoplastic mobility. In a subsequent study on absorption of triclopyr by tanoak, greater amounts were absorbed by immature leaves than mature leaves and by abaxial surfaces containing large stomatal densities than by axial surfaces (16).

No data are available on the metabolic degradation (if any) of triclopyr in plants.

#### 3.2 FATE IN SOIL

In general the fate of a pesticide in soil can be described in terms of six factors: volatilization, photodecomposition, adsorption/leaching, runoff, and chemical and microbial degradation. Although actual field data are

unavailable, volatilization is not considered to be a significant contributor to the loss of triclopyr following application because of the very low volatility of triclopyr (see Section 2.0). No data are available on the photodegradation (if any) of triclopyr in soil. However, based on photodegradation data for water (see Section 3.3), it is likely that photodegradation of triclopyr may occur in soil and from foliar surfaces. The adsorption/leaching and degradation data which have been submitted by Dow to EPA in support of registration applications for various uses of triclopyr are discussed in the following sections.

### 3.2.1 Adsorption, Leaching and Runoff

Triclopyr is considered a mobile herbicide (9). It is rapidly and reversibly adsorbed on soil particles. The extent of adsorption is primarily a function of soil type. Soil organic matter is the principal soil parameter responsible for adsorption, with increasing soil organic matter resulting in increased adsorption (9). Several laboratory studies have been conducted on the adsorption of the  $^{14}\text{C}$  labelled triethylamine salt of triclopyr by 12 soils (17). The organic carbon content of the soils ranged from 0.081 percent to 21.7 percent. Adsorption coefficients  $K_d$  and  $K_{oc}$  were measured and ranged from 0.016 to 14.5, and 12 to 78, respectively, indicating mobility. In a study using 3 soil types, the principal degradation product of triclopyr (trichloropyridinol) was found to have  $K_d$  and  $K_{oc}$  adsorption coefficients of 0.63 to 5.64 and 114 to 156, respectively, indicating low-to-intermediate mobility (18). No quantitative data are available on the effects of pH on triclopyr adsorption; because of its weakly acidic character, however, adsorption is expected to be favored under acidic conditions.

The adsorption capacity of a given soil type affects the potential for leaching of the herbicide from soil. Based on available limited data, it appears that triclopyr is leachable but that leaching should be less pronounced in soils with high organic matter content than in soils with lower organic matter content. Results of a leaching study using a low organic matter content soil (loam sand, 0.62 percent organic carbon) leached with 0.5 inches of water per day for 45 days showed that 75 percent to 80 percent of the triclopyr leached through the 12-inch soil column between days 11-15 (19). The trichloropyridinol degradate was found to be significantly less

leachable; while the triclopyr moved through the column after about 7.5 inches of water were applied, the degradate required 13 inches of applied water to completely pass through the column. In a study of 6 soils under test plot field condition in 6 states, small amounts of triclopyr and its degradates were observed in the 6-12 inch and 12-18 inch soil layers between 28 and 56 days following application of Garlon 3A at a rate of 3 gallons/acre and normal rainfall conditions (20). The trichloropyridinol degradate was less leachable and showed maximum residues in the 0 to 6 inch soil layer between 28 and 56 days after application and declined thereafter. The trichloromethoxy pyridine degradate remained around 0.1 ppm or less at all sample intervals. The six soil types tested were Tifton, Georgia loamy sand; Fargo, ND clay; Corvallis, or hazelaire complex; Benchley, TX clay to clay loam; Arthurdale, WV unspecified soil; and Laramie, WY Forelli fine sandy loam.

Because of its mobility and rapid desorption from soil particles, some loss of triclopyr due to solubilization and/or runoff may be expected following field application after rainfall. This was confirmed by results of several small-scale water monitoring programs in which residues of 6 ppb were observed in runoff water 5 months after application and 1 ppb was observed 9 months after application of 3 lb/acre triclopyr as the triethylamine salt, and after 150 cm of natural rainfall (21).

### 3.2.2 Chemical and Microbial Degradation

Triclopyr is not considered a persistent compound in soils. Laboratory studies have shown that triclopyr is decomposed quickly by soil microorganisms (9,14). Microbial degradation results in the formation of 3,5,6-trichloro-2-pyridinol and trichloromethoxypyridine (9,22). The average half-life in soil is 46 days with the actual value dependent on soil type and climatic conditions (14). Studies on the aerobic soil degradation of radio-labelled triclopyr indicated degradation to trichloro-2-pyridinol with a half-life between 79 and 156 days at 15°C, and less than 50 days at 25-35°C (9,22,23). The trichloro-2-pyridinol subsequently degraded to trichloromethoxypyridine, and eventually to CO<sub>2</sub> with 7 to 30 percent evolution of CO<sub>2</sub> at 375 days. Half-lives of these secondary reaction products and the degradation mechanisms have not been determined. The microbial degradation of

triclopyr was shown to be approximately 5 to 8 times slower under anaerobic conditions (i.e., waterlogging) than under aerobic conditions in a study using Illinois silty clay loam and Mississippi silt loam at 25°C (24).

Trichloropyridinol degradation has been shown to yield mostly carbon dioxide and some trichloromethoxypyridine (25). Tests with 15 soils from 10 major agricultural areas have indicated a half-life of 8 to 279 days for trichloropyridinol. Twelve of the 15 soils showed half-lives of less than 90 days. Two unidentified degradates were found at 1.8 to 6.5 percent of the initial radiolabelled trichloropyridinol. When the other degrade of triclopyr, trichloromethoxypyridine, was studied, results showed extensive degradation to carbon dioxide with estimated half-life of 50 days in two soils (Commerce silt loam and Flanagan silty clay loam), but more than 300 days in another soil (Yoho loam) (26). Trichloropyridinol was also found as a degrade of trichloromethoxypyridine.

In a study by Norris, et al. (27) of the fate of triclopyr on small hillside pastures in southwestern Oregon applied at a rate of 3.36 kg/ha, triclopyr residues were 350, 172, and 65 ppb at 6, 9, and 12 months after application, respectively.

Degradation of triclopyr in soil does not occur to any appreciable extent via chemical hydrolysis or other chemical routes (9). Laboratory studies using a silt loam soil have indicated that triclopyr does not degrade in sterile soil, but does degrade rapidly in the same soil when it is not sterilized (28).

### 3.3 PERSISTENCE IN WATER

Several laboratory studies conducted on the persistence and degradation of triclopyr in water have indicated triclopyr is stable to hydrolysis in buffered solutions for periods up to 9 months at pH 5, 7, and 8 and at 15, 25, and 35°C (29). Several photodegradation products, including 3,5,6-trichloro-2-pyridinol and 2-methoxy-3,5,6-trichloropyridine, were formed in minor amounts (less than one percent). Chemical hydrolysis is thus not expected to be a major pathway of triclopyr degradation in the aqueous environment.

The rate of triclopyr photodegradation in water is rapid in both natural sunlight and in the laboratory; half-life is 10 hours in water at 25°C (14,



30). The first degradation product is trichloropyridinol, which is rapidly degraded to various pyridine polyols formed via photolytic hydrolysis of the ring chlorine atoms (30). These primary and secondary photoproducts are further degraded in the aquatic environment. Thus, photodegradation is a major pathway for the dissipation of triclopyr in aquatic environments.

#### 4.0 IMPACTS ON NON-TARGET PLANTS AND ORGANISMS

At high application rates, triclopyr can cause injury to conifers and is not generally recommended for conifer release. In a study of the aerial applications of triclopyr and other herbicides in spruce-fir forests of Maine (31), Carlon 3A applied at a rate of 4.4 kg/ha caused minor injury to a small percentage of conifers, but at a rate of 2.2 kg/ha caused no injury. Injury to conifers following triclopyr applications have also been reported in the Pacific Northwest and in Sweden (5,32).

Triclopyr also exhibits some toxicity to agricultural crops, depending on application rates. Triclopyr applied at a rate of 0.5 lb a.i./acre showed some inhibition of cucumber yields over periods of at least 3 months following application, while rates of 3.0 and 9.0 lbs a.i./acre showed 50 percent inhibition of cucumber yields after a period of at least 4 months (33). Triclopyr applied at a rate of 0.5 and 1 ounce acid equivalents/acre had very little noticeable effect on wheat and no noticeable effect in bean stands planted 3, 8, 12, and 17 weeks after treatment (9). In general, most broad-leaf crops will tolerate small quantities of triclopyr to a greater extent than other auxin-type herbicides (14).

Since triclopyr is rapidly degraded by soil microorganisms, there would not be sufficient residue carryover to cause injury to susceptible species in the next growing season (8).

#### 4.1 FISH

Both triclopyr and the amine salt formulation Carlon 3A have very low toxicity to fish and lower aquatic organisms (see Table 1). No data are available on the fate and degradation products of triclopyr in fish or lower aquatic organisms.

TABLE 1. AQUATIC TOXICITY (96-HR AND 48-HR LC<sub>50</sub>'s) OF TRICLOPYR AND GARLON 3A (8,14)

Species	Exposure	Triclopyr	Garlon 3A
Bluegill	96 hr	148 ppm	891 ppm
Rainbow trout	96 hr	117 ppm	552 ppm
Oysters	48 hr	---	56-87 ppm
Shrimp	96 hr	---	895 ppm
Crab	96 hr	---	>1,000 ppm

#### 4.2 ANIMALS

Based on tests with laboratory animals, both triclopyr and its formulations are considered to have low toxicities to warm-blooded animals (see Table 2).

TABLE 2. ACUTE TOXICITY (ORAL LD<sub>50</sub> AND LC<sub>50</sub>) OF TRICLOPYR AND ITS FORMULATIONS TO LABORATORY ANIMALS (8,14,34)

Species	Triclopyr	Garlon 3A	Garlon 4
<b>LD<sub>50</sub></b>			
Rat (female)	630 mg/kg	2,140 mg/kg	2,140 mg/kg
Rat (male)	729 mg/kg	2,830 mg/kg	2,460 mg/kg
Rabbit (mixed)	550 mg/kg	---	---
Guinea pig	310 mg/kg	---	---
<b>LC<sub>50</sub></b>			
Mallard duck	>5,000 ppm	>10,000 ppm	>10,000 ppm
Japanese quail	3,278 ppm	---	---
Bobwhite quail	---	11,622 ppm	9,026 ppm

Dosages of triclopyr of 30 mg/kg/day produced no carcinogenic effects in mice and rats (34). Triclopyr was found to be non-mutagenic in dominant lethal and host mediated assay tests (34). It is considered mildly fetotoxic, exhibiting a reproductive toxicity effect at 200 mg/kg/day (34).

No data are available on the insecticidal activity of triclopyr on beneficial insects.

#### 4.3 SOIL MICROORGANISMS

Triclopyr is non-toxic to soil microorganisms. In a laboratory study of the effect of 500 ppm of triclopyr on 6 soil microorganisms (Aerobacter aerogenes, Pseudomonas aeruginosa, Salmonella typhosa, Staphylococcus aureus, Aspergillus terreus, and Pullularia pullulans), growth of the microorganisms was compared to controls (35). After 72 hours of incubation, no apparent effect was observed. The results of laboratory and field studies by Hallborn and Bergman (36) showed that treatment of Peltigera praetextata lichen and its free-living psycobiant algae Nostoc sp. with Garlon 3A at rates typically used in forestry applications did not significantly affect the rates of nitrogen fixation by either organism.

#### 4.5 BIOACCUMULATION

Triclopyr and its degradates trichloropyridinol and trichloromethoxy-pyridine do not accumulate to any appreciable extent in fish. Several laboratory studies have indicated that these compounds do not accumulate in edible portions of catfish or in fish heads, viscera or skins (37). Mosquito fish also do not accumulate significant residues of trichloropyridinol (37).

No data are available on the bioaccumulation of triclopyr in animals or microorganisms.

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